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Analysis for Ozone and Residual Chlorine by Differential Pulse Polarography of Phenylarsine Oxide

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16. ABSTRACT

The differential pulse polarography of phenylarsine oxide (C_6H_5AsO) as an indirect determination of ozone and residual chlorine is investigated. This procedure is compared with the standard methods of analysis for these oxidants in water and wastewater. The limit of detection for free chlorine at pH 7 is 3.3 ppb of Cl, 1.6 ppb of Cl for total chlorine at pH 4, and 2.5 ppb of O_3 at pH 4. The described method offers the advantage of fixing free chlorine in the field.

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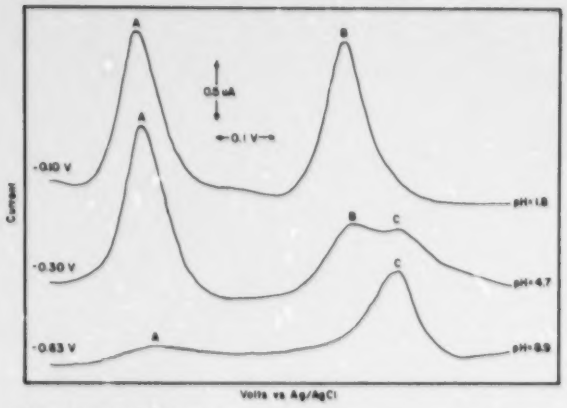

Figure 1. DPP of PAO at various pH values
[PAO] = 3.08×10^{-6} M; scan rate = 2 mV/s; drop time = 2 s; pulse amplitude = 100 mV; μ = 0.025; buffer compositions are HCl–$HC_2H_3O_2$–KCl at pH 1.8 and 4.7, and H_3BO_3–$Na_2B_4O_7$ at pH 8.9.

Marks et al. (*2*). The use of dual polarized platinum electrodes for end-point detection in chlorine analysis was suggested by Morrow (*3*). However, it has been shown that free chlorine residuals can cause a film-type polarization to occur at the surface of the platinum measuring electrode, resulting in lower sensitivity (*4, 5*). This problem can be minimized by allowing the electrodes to soak in an iodine solution before use. The addition of iodide to the sample was found to give better sensitivity for free chlorine analysis, yet this will cause interference from monochloramine.

An alternative to the use of PAO as the titrant in ozone and chlorine analysis is the addition of a known amount of PAO to the sample followed by back-titration with an oxidant (e.g., iodine). The end point is detected electrochemically by an increase in diffusion current due to excess oxidant. Adding excess PAO has the advantage of immediately quenching reactions involving the oxidants, preventing effusion or decomposition prior to or during analysis, suggesting the possible advantage of fixing free chlorine in the field. However, if iodine is the back titrant, monochloramine will still be included in the free chlorine analysis.

The technique developed below was the result of a search for an alternative approach to the back titration with iodine. The most obvious approach was a direct measurement of PAO. If an excess of PAO is added to the sample containing the oxidant, both phenylarsonous and phenylarsonic acids will be present. Polarography has been used for the specific quantitative measurement of mixtures of these acids (*6, 7*). The concentration of oxidant can be determined by the difference between PAO added to the sample and the amount remaining after the addition. We found differential pulse polarography (DPP) to be a sensitive method for PAO analysis. The optimization of the instrumental artifacts (*8*) resulted in a superior method whose sensitivity was pH dependent. The details of the electrochemical reduction of PAO by DPP have been reported elsewhere (*9*). Typical polarograms of PAO at different pH values, shown in Figure 1, exhibit three different peaks, A, B, and C.

This paper describes the use of the DPP of PAO as an indirect determination of residual chlorine and ozone and compares it with commonly used volumetric methods. We have determined sensitivities and detection limits for these oxidants under representative sets of procedural conditions. The detection limits were in the lower parts per billion range. We were also able to determine the free chlorine after a sample had been fixed in the field, which is a clear advantage over conventional titrimetric methods.

Experimental

Apparatus. A Princeton Applied Research Corporation (PAR) Model 174 Polarographic Analyzer was used with a Model 174/50 Drop Timer. All polarograms were recorded on either a Honeywell Model 194 strip chart recorder or a Houston Omnigraphic x–y plotter. A dropping mercury electrode (DME) with a natural drop time of 3 s at 49.5 cm with a flow of 3.05 mg/s was used for all experiments. A double vycor junction Ag|AgCl reference and a platinum counter electrode were used in a potentiostatic arrangement.

Dual platinum electrodes were used for amperometric titrations. A PCI Ozone Corporation Model C2P-6C ozonator was used for ozone production.

Reagents. All chemicals were reagent grade. All water was passed through mixed bed ion exchange resins and triple glass distilled prior to use. Triple-distilled mercury was used throughout. PAO stock solution (2.5×10^{-3} M) was prepared according to standard methods (*1*).

Procedures. Polarographic Analysis. Differential pulse polarography was used for all determinations, using standard polarographic techniques. Sample aliquots (5–20 mL) were scanned cathodically at 5 mV/s with a modulation amplitude of 100 mV and a drop time of 0.5 s. A scan rate of 2 mV/s and drop time of 2 s were optimum conditions and should be used when working at very low PAO levels. However, the higher scan rate and drop time can be used to decrease the analysis time for routine analysis. Adjustment of pH and addition of KI followed the standard amperometric titration procedures (*1*), except that excess PAO was added to the sample. The analyses were performed using: (a) −0.35 V initial potential and peak A at pH 7.5 for free chlorine; (b) −0.1 V initial potential and peak B at pH 4.0 for total chlorine; and (c) −0.1 V initial potential and peak A at pH 4.0 for ozone.

Volumetric Analysis. Ozone. Method A: The standard volumetric method for analysis of ozone (*1*) was used. This included the addition of iodide, the acidification of the sample, and the titration of the liberated triiodide with thiosulfate, utilizing a starch indicator. Method B: Excess PAO was added to the sample and back-titrated with iodine using a starch indicator.

Residual Chlorine. Free chlorine was determined at pH 7.5 using PAO titrant and an amperometric end-point detection. Total chlorine was similarly examined, except that excess KI was added at pH 4.0 (*1*).

Results and Discussion

Effect of pH. Typical polarograms of PAO at three different pH values are shown in Figure 1. At low pH, peak B is predominant, and at high pH peak C predominates, while at about pH 4.7 peaks B and C approach equal height. Better resolution could not be obtained with slower scan rate or smaller modulation amplitudes. The dependence of peak height on pH for all three peaks is shown in Figure 2 and points out the need for strict control of sample pH during the analysis.

Effect of Iodide. The effect of iodide addition on the DPP of PAO at pH 7.5 is shown in Figure 3. The concentration of iodide (0.0024 M) and the pH were the same as the standard method for chlorine analysis (free and monochloramine). The addition of iodide had no effect on E_p for any of the peaks at pH 7.5. However, peak A appeared on the shoulder of a peak assumed to involve the iodide. Figure 3 also shows the effect of iodide at pH 3.8. The concentration of iodide (0.0024 M) and pH were the same as the standard method for total chlorine analysis. At this pH the iodide peak completely obscured peak A, but quantitative measurements were made using peak B.

Detection Limit. The detection limit for the oxidant is

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■ The differential pulse polarography of phenylarsine oxide (C_6H_5AsO) as an indirect determination of ozone and residual chlorine is investigated. This procedure is compared with the standard methods of analysis for these oxidants in water and wastewater. The limit of detection for free chlorine at pH 7 is 3.3 ppb of Cl, 1.6 ppb of Cl for total chlorine at pH 4, and 2.5 ppb of O_3 at pH 4. The described method offers the advantage of fixing free chlorine in the field.

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Standard methods for the determination of free and combined chlorine in water and wastewater employ a direct titration of the oxidant using phenylarsine oxide (PAO) as the titrant (*1*). PAO can also be used in place of sodium thiosulfate in the analysis of dissolved ozone (*1*). Existing in solution as phenylarsonous acid, the use of this reagent is based on the oxidation of As(III) to As(V) (phenylarsonic acid). The end point of these titrations can be determined colorimetrically, using starch–iodide, or amperometrically, using a variety of electrode combinations. Both detection methods are based on the presence of an oxidant (free chlorine or iodine).

The determination of residual chlorine in sewage using PAO with amperometric end-point detection was first reported by

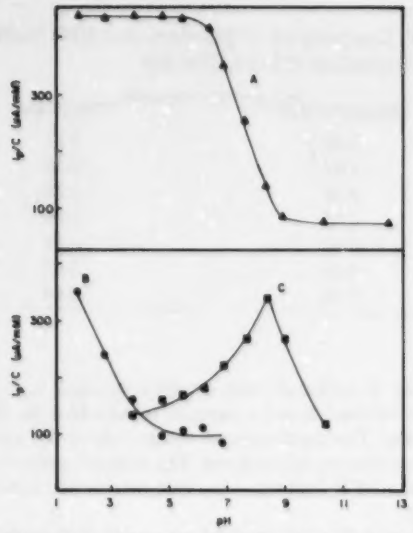

Figure 2. Dependence of peak current for peaks A, B, and C on pH
[PAO] = 3.69×10^{-6} M; scan rate = 2 mV/s; drop time = 2 s; pulse amplitude = 100 mV; μ = 0.025

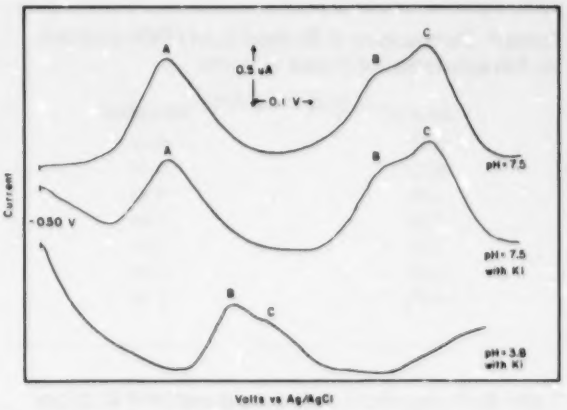

Figure 3. The effect of iodide on the DPP of PAO
[PAO] = 3.08×10^{-6} M; scan rate = 2 mV/s; drop time = 2 s; pulse amplitude = 100 mV; μ = 0.025

Table I. Comparison of Method A and DPP Methods for Determination of Ozone in Water

ozone concn, ppm	
method A	DPP method
0.60	0.60
0.66	0.77
1.05	1.14
1.19	1.43
1.84	1.96
1.98	1.93
2.23	1.91
2.44	2.00

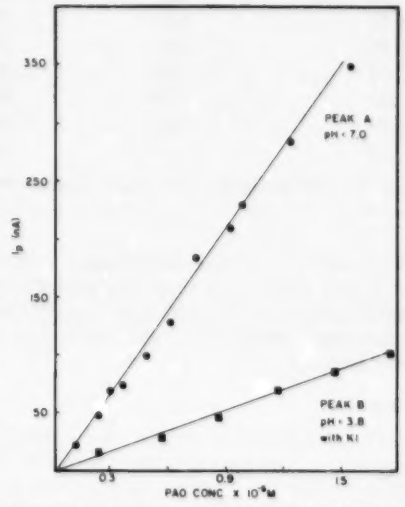

Figure 4. Calibration curves for 0.123–1.75 $\times 10^{-6}$ M PAO
Scan rate = 2 mV/s; drop time = 2 s; pulse amplitude = 100 mV; μ = 0.025

based on the ability to distinguish differences in the measured current for a given PAO concentration. One can detect an oxidant concentration that decreases the signal by a statistical multiple of the standard deviation of the measured current for the original PAO concentration.

Using peak B at pH 4 and 0.0024 M KI, the peak current for a PAO concentration of 1.54×10^{-6} M was 105 nA. The standard deviation was calculated to be 1 nA from seven replications of this PAO concentration; therefore, a total chlorine concentration that caused a decrease in the peak current three times the standard deviation would represent the limit of detection for that oxidant. A 3-nA decrease would represent a difference in PAO concentration of 4.4×10^{-8} M and this change is equivalent to a total chlorine concentration of 1.6 ppb of Cl.

A calibration curve using peak A prepared under free chlorine analysis conditions (*1*) is shown in Figure 4. The peak current for PAO (1.8×10^{-6} M) was 421 nA, with a standard deviation of 7.2 nA determined from seven replications. In a similar manner as above, the difference in PAO concentration was found to be 9.2×10^{-8} M, which is equivalent to 3.3 ppb of Cl.

At pH 4 with no iodide, conditions for ozone analysis, peak A will have an I_p/C ratio of 440 μA/mM as shown in Figure 2. For a PAO concentration of 1.8×10^{-6} M, the peak current was 792 nA with a standard deviation of 7.8 nA. The difference in PAO concentration represented by three times this standard deviation is 5.3×10^{-8} M and this is equivalent to an ozone concentration of 2.5 ppb.

All of the above detection limits were found using a scan rate of 2 mV/s, a modulation amplitude of 100 mV, and a drop time of 2 s; the optimum analysis conditions as previously reported (*9*).

Correlation with Other Analytical Methods. The results obtained from the DPP of PAO for ozone analysis were compared with two volumetric methods. To compare the results of DPP and the standard method A, parallel samples of different ozone concentration were analyzed, and these data are given in Table I. The average correlation was calculated to be 1.02 with a standard deviation of 0.13. The results presented in Table II compare DPP with volumetric method B, and the average correlation of 1.03 ± 0.04 was calculated.

The comparison of DPP and the standard method for total residual chlorine is shown in Table III for tap water (TW), sewage treatment plant effluent (STP), and river water at a treatment plant outfall (RW). Two-liter samples were obtained, and parallel determinations were again done. The average correlation was 1.02 ± 0.06.

Table IV is a comparison of the DPP method with the standard method for free chlorine analysis of tap water. The average correlation was 1.07 ± 0.14. The addition of excess PAO offers the advantage of quenching the oxidants, thereby preventing loss of free chlorine (or ozone) by stirring. This

Table II. Comparison of Method B and DPP Methods for Determination of Ozone in Water

ozone concn, ppm	
method B	DPP method
0.17	0.18
0.74	0.74
1.03	1.11
1.93	1.96
2.07	2.25
2.60	2.62
3.04	3.02

Table III. Comparison of Standard and DPP Methods for Determination of Total Chlorine

total chlorine concn, ppm		
standard method	DPP method	sample
0.58	0.55	TW[a]
0.70	0.65	TW
0.75	0.81	TW
1.00	1.06	RW[b]
1.03	1.06	RW
1.23	1.29	STP[c]
1.29	1.32	STP

[a] TW, tap water. [b] RW, river water. [c] STP, sewage treatment effluent.

suggests the possibility of fixing free chlorine in the field for analysis at a later time. A tap water sample was buffered to pH 7.5, and PAO was added resulting in 1.3×10^{-6} M excess. This sample was analyzed after 24 h and was found to be 99.5% of the initial finding.

Conclusions

The above comparisons of methods show that the DPP technique compares very well with the standard methods for both ozone and chlorine. The direct measurement of PAO by DPP offers the advantage of fixing and storing samples for free chlorine and ozone, while this cannot be accomplished using conventional standard methods.

The parts per billion measurements for total chlorine, ozone, and free chlorine using DPP of PAO are substantially better than the conventional standard methods. This excellent sensitivity is achieved with samples as small as 5 mL, as compared to the 0.2- to 1-L samples required for the standard procedures. The small sample volume offers the additional advantage of using less reagent. The analysis time and precision of the DPP technique are comparable to the standard methods.

Table IV. Comparison of Standard and DPP Methods for Determination of Free Chlorine

free chlorine concn, ppm	
standard method	DPP method
0.23	0.27
0.27	0.31
0.36	0.37
0.50	0.40
0.52	0.52
0.52	0.61
0.56	0.64

As illustrated by the total chlorine analysis, if polarographic interferences occur at one peak, the alternate peak can be used for quantification. Since the E_p for both peaks is pH dependent, this offers further versatility in eliminating possible interfering peaks. No apparent polarographic interferences were observed in the water samples examined. The residual PAO concentration may be kept sufficiently large to make most background errors insignificant.

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